

光里白中的两个新苷类成分

李明明^{1,2}, 王扣^{1,2}, 陈宣钦^{1,2}, 彭丽艳¹, 成晓¹, 赵勤实¹

(1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室,
云南 昆明 650204; 2 中国科学院研究生院, 北京 100049)

摘要: 从光里白 (*Diplopterygium laevissimum*) 的 95% 乙醇提取物中分离得到 2 个新的苷类成分, 经波谱手段鉴定了其结构, 命名为 hymenoside X (1) 和 hexanoside A (2)。

关键词: 里白科; 光里白; 苷类成分; hymenoside X; hexanoside A

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Two New Glycosides from *Diplopterygium laevissimum* (Gleicheniaceae)

LI Ming-Ming^{1,2}, WANG Kou^{1,2}, CHEN Xuan-Qin^{1,2}, PENG Li-Yan¹,
CHENG Xiao¹, ZHAO Qin-Shi^{1**}

(1 State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming

Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China;

2 Graduate University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: Two new glycosides hymenoside X (1) and hexanoside A (2), were isolated from the 95% EtOH extract of *Diplopterygium laevissimum*. Their structures were determined by extensive spectroscopic analysis.

Key words: Gleicheniaceae; *Diplopterygium laevissimum*; Glycosides; Hymenoside X; Hexanoside A

Diplopterygium laevissimum (Christ) Nakai, belonging to the Gleicheniaceae family, is widely distributed in the northwest of Yunnan Province, China [Kunming Institute of Botany, Chinese Academy of Sciences, 2006]. To our knowledge, no phytochemical investigation on this species has been reported. In our previous research on Gleicheniaceae family, we have reported two highly oxygenated phenolic derivatives and some diterpene glycosides (Li *et al.*, 2006, 2007, 2008; Zhang *et al.*, 2009). As a continuation of our systematic research work on the bioactive constituents from fern, the aerial parts of *D. laevissimum* had been

studied and two new compounds were isolated. We herein report the isolation and structure elucidation of compounds 1 - 2.

Results and Discussion

Compound 1 was obtained as amorphous powder, and its molecular formula was elucidated as C₂₁H₂₆O₁₀ based on the negative HR-ESI-MS ([M-H]⁻ at *m/z* 437.1460; calcd for C₂₁H₂₅O₁₀, 437.1447), requiring nine degrees of unsaturation. The IR spectrum showed the absorption bands for the hydroxyl (3 427 cm⁻¹) and carbonyl groups (1 708 cm⁻¹), and the absorp-

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Author for correspondence; E-mail: qinshizhao@mail.kib.ac.cn; Tel: +86-871-5223058

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作者简介: 李明明 (1984-) 男, 在读硕士研究生, 主要从事蕨类植物化学研究。

tions at $1\,605\text{ cm}^{-1}$, $1\,515\text{ cm}^{-1}$ and $1\,447\text{ cm}^{-1}$ suggested it might have an aromatic ring group. The ^{13}C and DEPT NMR spectra of **1** exhibited the presence of a glucose moiety [δ_{C} 62.6 (t), 77.7 (d), 71.8 (d), 75.9 (d), 74.5 (d) and 100.5 (d)], a *p*-coumaroyl group [δ_{C} 166.6 (s), 115.6 (d), 145.6 (d), 127.0 (s), 2×130.9 (d), 2×116.6 (d) and 160.5 (s)]. The double bond of *p*-coumaroyl group was suggested as *trans*-due to the big coupling constant ($J = 16.0\text{ Hz}$). Assignment of glucosidic protons system were achieved by analysis of ^1H - ^1H COSY and HSQC experiments. The other six carbon signals including these characteristic NMR data: one carbonyl (δ_{C} 169.3), two methylenes (δ_{C} 36.4, 36.0), two oxygenated methines (δ_{C} 71.1, 72.8), and one methyl group (δ_{C} 21.6), suggested the aglycone might be a γ -pyrone type compound. From ^1H - ^1H COSY and HMBC correlations we confirmed the aglycone was 3-hydroxy-5-hexanolide. HMBC correlations between the anomeric proton H-1 (δ_{H} 4.72) of glucopyranosyl unit and C-3 (δ_{C} 71.1) of the aglycone showed glucopyranosyl unit was linked to C-3, and H-2 (δ_{H} 4.83) had HMBC correlations with C-9 (δ_{C} 169.3) showed the *p*-coumaroyl group was linked to C-2.

The ^1H and ^{13}C NMR spectra of the aglycone was similar to those of (3*R*, 5*R*)-3-(β -D-glucopyranosyloxy)-5-hexanolide, whose absolute structure was established by X-ray crystallographic analysis of its *p*-bromobenzoate derivative (Toyota *et al.*, 2001). And by comparison the optical rotation value of **1** with the reported analogue hymenoside U [$[\alpha]_{\text{D}}^{22} = -29.0$ ($c = 2.80$, MeOH) (Toyota *et al.*, 2002), the absolute

configuration of **1** was deduced to be (3*R*, 5*R*). Consequently, the ultimate structure of **1** was elucidated as showed in Fig. 1 and named as hymenoside X.

Compound **2**, obtained as amorphous powder, had a molecular formula of $\text{C}_{22}\text{H}_{30}\text{O}_{11}$ determined by the negative HR-ESI-MS ($[\text{M}-\text{H}]^-$ at m/z 469.1712; calcd for $\text{C}_{22}\text{H}_{29}\text{O}_{11}$, 469.1709), requiring eight degrees of unsaturation. The NMR data also suggested the exist of one glucose moiety and a (*E*)-*p*-coumaroyl group. Compared with compound **1**, compound **2** had one more methoxyl and one less degree of unsaturation, it was deduced to be a ring opened γ -pyrone-type compound. HMBC correlations between the methoxyl protons (δ_{H} 3.52) and C-1 (δ_{C} 172.0) of the aglycon showed methoxyl unit was linked to C-1. Compound **2** related to **1** and might be produced from **1** during the use of methanol (Toyota *et al.*, 2002). Thus, structure of **2** was elucidated and named as hexanoside A.

Experimental

General Optical rotation was measured on a Horiba SE-PA-300 polarimeter. IR spectra was obtained with a Tensor 27 FT-IR spectrometer with KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on Bruker AV-400 and DRX-500 spectrometers in CD_3COCD_3 at room temperature (δ in ppm, J in Hz). FAB-MS was carried out on a VG Autospec-3000 spectrometer. HR-ESIMS was recorded with an API QSTAR Pulsar i spectrometer. Silica gel (200-300 mesh), Silica gel H (Qingdao Marine Chemical Ltd., China) and LiChroprep RP-18 silica gel (40-63 μm , Merck, Dramstadt, Germany) were used for column chromatography. Fractions were monitored by TLC and spots were visualized by heating silica gel plates immersed with 15% H_2SO_4 in ethanol. Solvents were distilled prior to use.

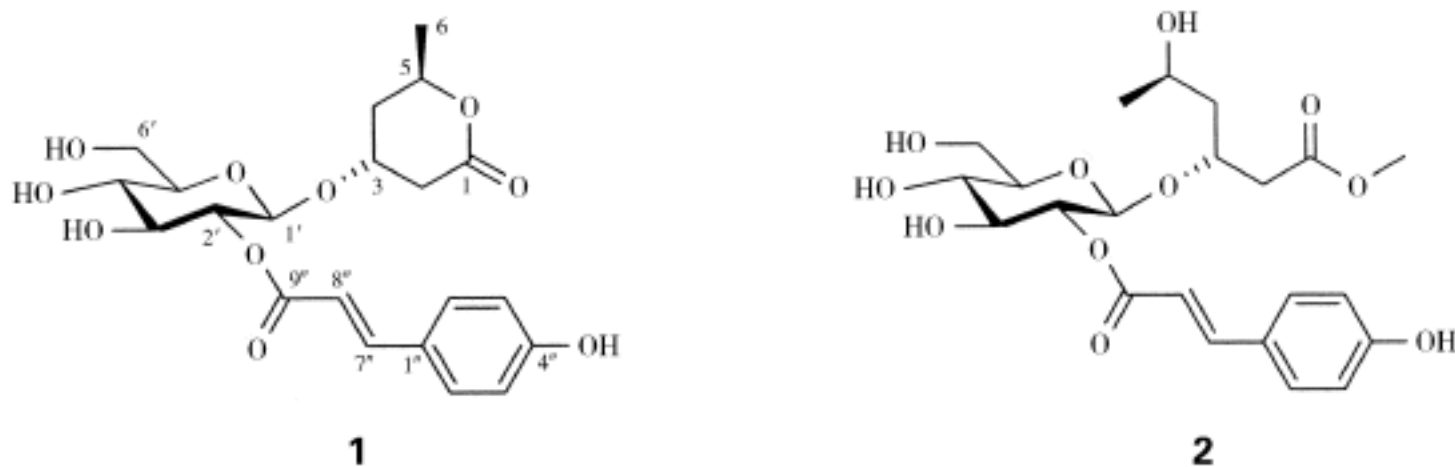


Fig. 1 The structures of **1** and **2**

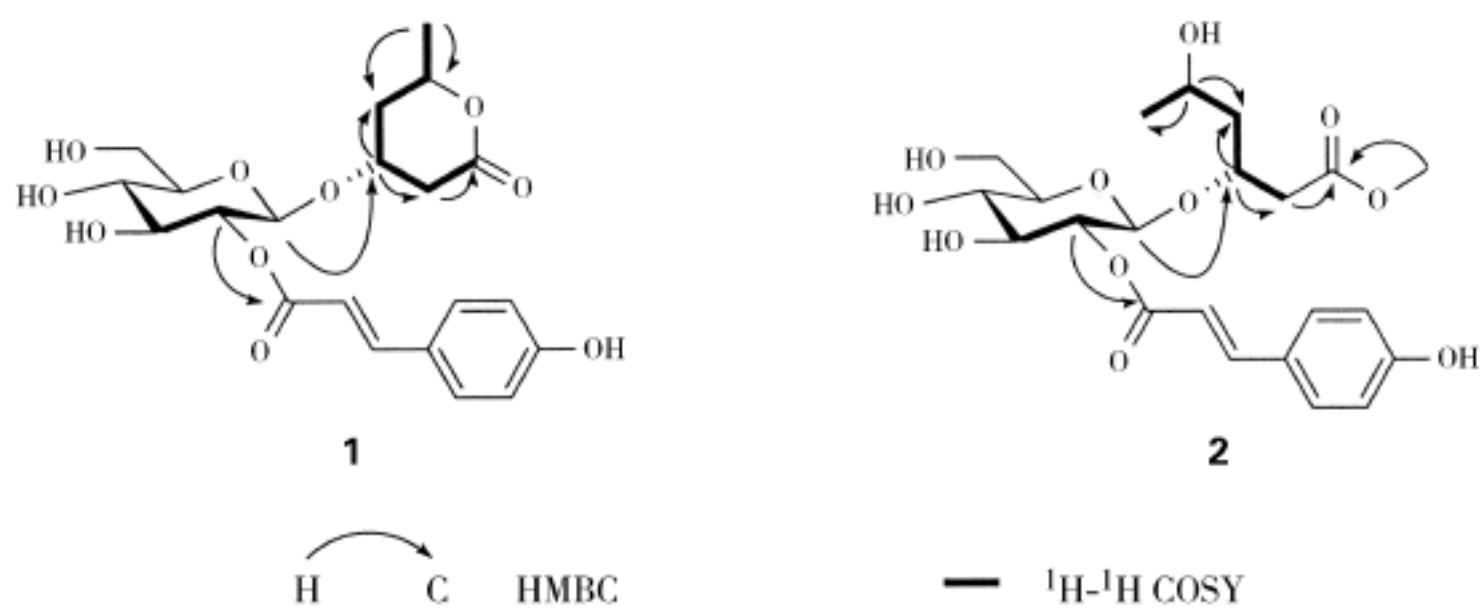


Fig . 2 Key ¹H-¹H COSY and HMBC correlations of compounds 1 and 2

Preparative HPLC was performed on a Shimadzu LC-8A preparative liquid chromatograph with Shimadzu PRC-ODS (K) column . Sephadex LH-20 (Amersham Pharmacia biotech, Sweden) .

Plant material The aerial parts of *Diplopterygium laevissimum* (Christ) Nakai were collected from Pingbian, Yunnan Province, China in July 2007 and identified by professor Cheng Xiao at Kunming Institute of Botany, Chinese Academy of Sciences . A voucher specimen (No . 200707A03) has been deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences .

Extraction and isolation The dried and powdered plant materials (2.6 kg) were extracted with 95 % EtOH (12 L, each 2 d) for three times . After evaporation of the solvent in vacuo, the concentrate was suspended into H₂O and partitioned successively with EtOAc . The EtOAc extract (100 g) was chromatographed on a silica gel column, eluting with CHCl₃ MeOH (1 0 to 5 5) to give five fractions (Fr . 1—Fr . 5) . Fr . 2 was further subjected to column chromatograph over silica gel (CHCl₃ MeOH 9 1) and Sephadex LH-20 (MeOH) , then purified semi-HPLC (MeOH H₂O 38 62) to get 1 (6 mg) and 2 (7 mg) .

hymenoside X (1): amorphous powder; [α]_D^{18.8} = -42.1

Table 1 ¹H and ¹³C NMR data for compounds 1 and 2 in CD₃COCD₃ . in ppm, *J* in Hz .

NO.	1		2	
	(C)	(H)	(C)	(H)
1	169.3 s		172.0 s	
2	36.0 t	2.54 (dd, 4.8, 17.6) 2.62 (ddd, 1.6, 3.2, 17.6)	40.5 t	2.45 (dd, 5.2, 16.0) 2.51 (dd, 7.6, 16.0)
3	71.1 d	4.34 (m)	75.7 s	4.26 (t, 8.0)
4	36.4 t	1.71 (ddd, 3.2, 11.6, 14.0) 2.13 (br d 14.0)	45.4 t	1.56 (dt, 4.0, 14.0) 1.82 (dt, 8.0, 14.0)
5	72.8 d	4.65 (m)	65.4 d	3.87 (m)
6	21.6 q	1.24 (d, 7.6)	24.1 q	1.10 (d, 6.4)
Glc-1	100.5 d	4.72 (d, 8.0)	101.8 d	4.69 (d, 8.0)
2	74.5 d	4.83 (t, 8.0)	74.5 d	4.77 (t, 8.0)
3	75.9 d	3.65 (m)	76.0 d	3.59 (m)
4	71.8 d	3.44 (m)	71.9 d	3.39 (m)
5	77.7 d	3.41 (m)	77.6 d	3.38 (m)
6	62.6 t	3.86 (m), 3.44 (m)	62.8 t	3.86 (m), 3.66 (m)
1	127.0 s		126.9 s	
2 , 6	130.9 2 × d	7.53 (d, 8.4)	130.8 2 × d	7.54 (d, 8.4)
3 , 5	116.6 2 × d	6.92 (d, 8.4)	116.7 2 × d	6.88 (d, 8.4)
4	160.5 s		160.6 s	
7	145.6 d	7.60 (d, 16.0)	145.2 d	7.59 (d, 16.0)
8	115.6 d	6.31 (d, 16.0)	115.8 d	6.32 (d, 16.0)
9	166.6 s		166.5 s	
OCH ₃			51.7 q	3.52 (s)

($c = 0.11$, MeOH); UV $_{\text{max}}^{\text{MeOH}}$ (log): 313 (4.12), 226 (3.88), 211 (3.87), 199 (3.87), 192 (3.86); IR $_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3426, 1708, 1632, 1605, 1515, 1447, 1384, 1263, 1172, 1070 cm^{-1} ; ^1H and ^{13}C -NMR: see Table 1; FAB-MS (neg.) $m\ z$: 437 $[\text{M-H}]^-$; HR-ESI-MS (neg.): 437.1460 $[\text{M-H}]^-$ ($\text{C}_{21}\text{H}_{25}\text{O}_{10}$; calcd .437.1447) .

hexanoside A (2): amorphous powder; $[\alpha]_{\text{D}}^{19.1} = -38.5$ ($c = 0.10$, MeOH); UV $_{\text{max}}^{\text{MeOH}}$ (log): 314 (3.95), 227 (3.70), 211 (3.69), 200 (3.70), 194 (3.66); IR $_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3427, 2926, 1716, 1632, 1605, 1515, 1440, 1265, 1172, 1075, 1033 cm^{-1} ; ^1H and ^{13}C NMR: see Table 1; FAB-MS (neg.) $m\ z$: 469 $[\text{M-H}]^-$; HR-ESI-MS (neg.): 469.1712 $[\text{M-H}]^-$ ($\text{C}_{22}\text{H}_{29}\text{O}_{11}$; calcd .469.1709) .

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